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# SPECTROPHOTOMETRIC DETERMINATION OF BORON IN ROCKS BY EXTRACTION WITH METHYLENE BLUE TETRA FLUOROBORATE COMPLEX /741*

Akinori Isozaki, Satori Utsumi**

ABSTRACT. A standard procedure for determining boron in rocks using acids is described.

Methylene blue tetrafuoroborate complex can be extracted with dichloroethane. Based on this finding, studies were made to establish a rapid method for the determination of minute quantities of boron in rocks.

When the rock is readily decomposable in mixed sulfuric and hydrofluoric acids, place 0.1 g sample, the mixed acid, and hydrogen peroxide in a polypropylene beaker, and heat on a water bath for 20 minutes. When the sample is decomposed, dilute the solution with water to 20 or 200 ml, depending on whether the boron content is less or more than 10 ppm 1 μg/0.1 g. Transfer all or part (20 ml) of the diluted solution to a polyethylene separatory funnel, add methylene blue and dichlorethane, and shake. After separating the organic layer, wash it with silver sulfate solution, and measure the absorbance at 660 mμ against dichloroethane. For those rocks which are difficult to dissolve with the mixed acid: Place the sample in a platinum crucible and fuse with sodium carbonate. Dissolve the mass in a polypropylene beaker with sulfuric acid, hydrofluoric acid, and hydrogen peroxide. Then follow the same procedure.

Other elements present in the rocks do not interfere with the analyses. With this method we were able to determine 0.5 ~ 100 ppm boron in rocks.

## 1. Introduction

Since boron in rocks is one of the important elements in geochemistry, a simple and rapid method of determination is desired.

Determination of boron in rocks relies mostly on spectrophotometric methods; there are relatively few colorimetric methods for the determination of boron, including those for boron in soils. Although, recently, curcumine (Ref. 1), and carmine methods (Ref. 2, 3) are mostly used, handling of the sample is difficult, and requires skill and time. The crystal violet method (Ref. 4) has low sensitivity. The determination of boron using methylene blue could not be found elsewhere.

The authors previously studied the spectrophotometric method by extraction of a minute quantity of boron (Ref. 5). Applying this method, we reported on the spectrophotometric determination of boron by extraction in natural water (Ref. 6). In order to apply these methods (Ref. 5, 6), we must first learn how to treat

*Note: Numbers in margin indicate pagination in the original foreign text.

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the samples before they are subjected to the extraction process. It is convenient to heat treat samples with sulfuric, and hydrofluoric acids, since upon decomposition, boron is converted to the tetrafluoro ion ($BF^{-4}$). For those samples which can not be decomposed by the acids, sulfuric and hydrofluoric acids were used after the alkaline fusion.

Decompose 0.1 g of sample by either method, extract boron as $BF_4$· methylene blue with dichloroethane, and measure the absorbance after washing the organic layer. Following such a procedure, we were able to determine 0.5 ~ 100 ppm boron in rocks in a relatively short time with good precision. /742

## 2. Experimental Results and Discussion

### 2.1 Reagent and Apparatus

Sulfuric Acid (2N): 57.4 ml of special grade concentrated sulfuric acid is diluted with water to 1 $l$.
Hydrogen Peroxide Solution (1%): Dilute 30% special grade hydrogen peroxide.
Non-hydrous Sodium Carbonate: Asahi Glass, standard reagent (99.99%)
Samples for the Standard Curve: Mix special grade non-hydrous silicic acid with calcium carbonate (7:1) in an agate mortar.

A 100 ml polypropylene beaker to decompose the sample; a 200 ml measuring flask; 10 ml pipette and stirring rod; a 20 ml platinum crucible.

### 2.2 Procedure and Standard Curves

Samples which are readily decomposable with sulfuric and hydrofluoric acid: Place 0.1 g sample in a 100 ml polypropylene beaker, and add 5 ml 1N sulfuric acid plus 5 ml of 5% hydrofluoric acid (which will be called mixed acid below). Add 1 ml of 1% hydrogen peroxide solution, and decompose by heating for 20 minutes on a water bath while stirring with a polyethylene rod. Cool to room temperature, and dilute to either 20 ml if the boron content is less than 10 ppm 1μg/0.1 g or 200 ml* if the content is more than 10 ppm in a polyethylene measuring flask. Then transfer 20 ml into a polyethylene separatory funnel. Add 3 ml of 0.001 mol/l methylene blue solution, and 10 ml of dichloroethane, and shake vigorously for 1 minute. When the two layers are separated, transfer the organic layer into a separatory funnel containing 5 ml of silver sulfate solution containing 1 mg as silver ion, and wash the organic layer by shaking vigorously for 1 minute. After allowing it to settle, measure the absorbance of the organic layer at 660 mμ in a 1 mm cell using dichloroethane as a reference. When the boron content is less than 10 ppm, use curve I, otherwise, use curve II of Fig. 1. Samples which are difficult to decompose with the mixed acid: Place 0.1 g sample in a platinum crucible, fuse with 0.5 g non-hydrous sodium carbonate for 20 minutes, and cool. Add 7 ml, 2N sulfuric acid, and transfer the crucible and the contents into a polypropylene beaker. Wash the crucible with a small amount of water, add 5 ml, 5% hydrofluoric acid and 1 ml, 1% hydrogen peroxide, and heat for 20 minutes on a water bath. Then follow the same procedure as described above.

Although a rock with known boron content should be used for the standard

*When a 200 ml measuring flask is not available, use a 100 ml one. In this case, take 10 ml, and dilute to 20 ml with water.

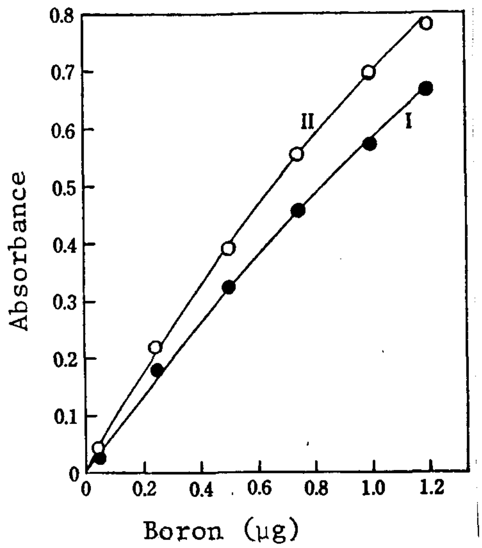

Figure 1. Standard Curves

curve, we were obliged to use 0.08 g of the previously described samples* for the standard curve, to which were added known amounts of the boron standard solution, since it is difficult to obtain such rocks. Standard curves were made by subtracting the absorbance of the blank from the actual absorbance (e.g. Fig. 1). Curve I was obtained by using the whole sample solution. And curve II was obtained when only part of the solution was taken from the total 200 ml (the difference will be discussed later). The curves have slight curvatures, but have good reproducibility. Although fused samples give higher absorbances, agreements are obtained when the blank absorbance is subtracted.

## 2.3 Examination of the Determination Conditions.

### 2.3.1 Decomposition of Sample:

When the sample for the standard curve was placed in a platinum crucible with sulfuric and hydrofluoric acids and heated on a sand bath, the absorbance of the blank became large, and the reproducibility became bad, depending on the temperature, and the length of the heating process. One sample was placed in a platinum crucible with only sulfuric acid, and heated. After it was cooled, it was transferred into a polyethylene separatory funnel with hydrofluoric acid, and allowed to stand at ambient temperature. The other sample was placed in a platinum crucible with sulfuric and hydrofluroic acids, and allowed to stand overnight at ambient temperature. In both cases, the absorbances of blanks were low and constant. A similar result was obtained using a brand new crucible or using phosphoric acid, instead of sulfuric acid. It is suspected that boron might have been leached from the platinum crucible. We will pursue the matter further in the future.

When the sample for the standard curve was placed in a polyethylene beaker instead of a platinum crucible, and heated on a water bath with sulfuric and hydrofluoric acids, the absorbance of the blank became higher with the heating time; the absorbance was 0.18 ± 0.02** when the heating time was **20~30** minutes.

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* The sample for the standard curve was decomposed with sulfuric, and hydrofluoric acids at ambient temperature in a polypropylene beaker. The amount of boron in the sameple was determined by the previously described method (Ref. 5). Since the value obtained was close to that of the blank (0.11 ±0.01), the amount of boron in the sample can be considered negligible. When boron is found in the samples for the standard curve, appropriate corrections must be applied.

** This is the same as the value for the blank in Curve I, Figure 1. In Curve II the absorbance is 0.11 ±0.01 because of the dilution (Ref. 5).

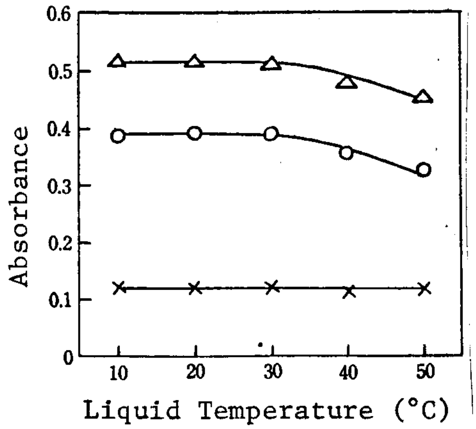


Figure 2. Effect of Extraction Temperature
X: Blank Value
Δ: 0.5 μg boron
O: 0.5 μg boron
Blank Value

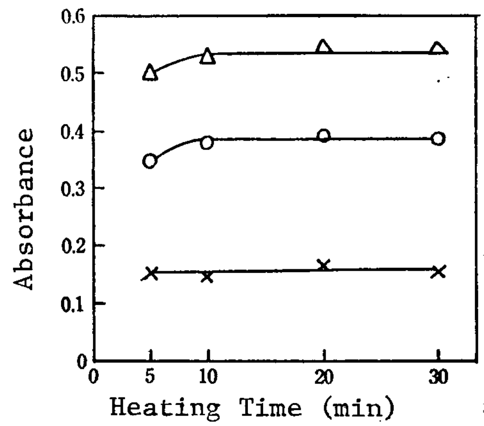


Figure 3. Formation of $BF_4^-$ and Volatilization of $BF_3$
X: Blank Value
Δ: 0.5 μg Boron
O: 0.5 μg Boron
Blank Experiment

Although boron is assumed to be leached from the polyethylene beaker, this is not certain. Polypropylene beakers (100 ml) which are sold as heat-resistant beakers are easier to handle than the polyethylene beakers.

Samples which are not decomposable by the mixed acid require alkaline fusion. The sample for the standard curve was placed in a platinum crucible with sodium carbonate and fused for 20~30 minutes. After fusion, it was allowed to cool, and sulfuric acid was added. Then it was transferred to a polypropylene beaker. Hydrofluoric acid, and hydrogen peroxide were added, and were heated for 20 minutes. Although the absorbance (0.23 ±0.02)* of the blank was slightly higher than that obtained with the blank which was decomposed in a polypropylene beaker with the mixed acid, a rather constant value was obtained. The absorbance of the blank did not increase in the case when sodium carbonate was fused in a platinum crucible, unlike the case when it was de- /743
composed by the acid in a platinum crucible (there is no leaching of boron). We will investigate the cause in the future.

When the concentration of the mixed acid is low, the rock is difficult to decompose. When the sample is heat-decomposed in a polypropylene beaker with a concentrated mixed acid, the absorbance of the blank increases, and the reproducibility becomes poor. When the hydrofluoric acid concentration increases, the slope of the standard curve flattens, and the sensitivity decreases (Ref. 5), which explains the difference in the standard Cruves I, and II in Figure 1. As a result, we decided to use 5 ml, 1N sulfuric acid, and 5 ml, 5% hydrofluoric acid. Twenty minutes of heating is ample for the easily decomposable sample. No effects were found from a longer heating of poorly soluble samples.

* Sodium carbonate contains boron.

Considering the boron content in the rocks, 0.1g was adopted as a sample weight.

### 2.3.2 The Effect of Extraction Temperature

Study was made on the effect of the temperature of dichloroethane on its extractability when the rock is decomposed, and converted to $BF_4^-$, and complexed with methylene blue. The effect of the temperature on the blank and 0.5 μg boron, following the previously reported procedure (Ref. 5), is shown in Figure 2.

The absorbance of the blank is unchanged with temperature. With 0.5μg boron, although the absorbance does not appreciably change up to 30°C, it decreases appreciably at higher temperatures. Therefore, the solution should be cooled with water to room temperature before subjecting it to extraction.

### 2.3.3 The Formation of $BF_4^-$ and the Volatilization of $BF_3$

In the previously reported procedure (Ref. 5), the formation of $BF_4^-$ required over 30 minutes at ambient temperature with 3 ml, 1N sulfuric acid, and 3 ml, 5% hydrofluoric acid. The formation in this case (new procedure), however, is considered to be accelerated, since it is heated on a water bath. There is a danger that formed $BF_4^-$ may escape as boron fluoride ($BF_3$) when it is heated.

Hence, the standard boron solution (0.5 μg boron) was placed in a polypropylene beaker with the mixed acid, and heated on a water bath. It was, then, cooled with water * to the ambient temperature, transferred into a separatory funnel, washed with a small amount of water, and made to equal a 20 ml volume. The same procedure (Ref. 5) was followed, and the absorbance measured (the blank was run, similarly). The results are shown in Figure 3.

If the absorbance (against blank) of 0.5 μg boron falls on the previously reported (Ref. 5) standard curve (absorbance is 0.39 ±0.01), then the formation of $BF_4^-$ is complete, and there is no loss of $BF_3$.

As indicated in Figure 3, the formation of $BF_4^-$ is rather fast compared to that of ambient temperature; the formation is complete with 10 minutes of heating, but not with 5 minutes of heating. Since the absorbance is unchanged whether the heating time is 20 or 30 minutes, the loss of $BF_3$ need not be considered with 30 minutes of heating.

Considering the time required for the formation of $BF_4^-$, and the decomposition of rocks, the heating time was set at 20 minutes.

* It required 10 minutes from the time it was cooled to the time it was extracted, which is not included in the heating time.

## 2.3.4 The Effect of the Coexisting Ions

A study on the effect of other elements, which are commonly found in rocks in quantities which are regarded as maximum amounts in a 0.1g sample, showed that none of such elements was found to cause interference.

However, since more than 5 mg of Fe(II) ion causes interference, 1 ml, 1% $H_2O_2$ solution was added to oxidize Fe(II). Moreover, although it is a minute amount, 0.01 mg of chromic acid will cause interference. Chromium in the rock is converted to the salt when fused with sodium carbonate. The solution was acidified, and the chromium ions were reduced to Cr(III) with hydrogen peroxide. As stated in the "Effect of Coexisting Ions" in the determination of boron in natural water (Ref. 6), the dichloroethane layer was washed with a silver sulfate solution (contains 0.1 mg of silver ions).

## 2.4 The Determination of Boron in Rocks

Table I shows the results of the analyses on several samples following procedure 2.2. The determined values of boron when samples are decomposed with the mixed acid (which will be called acid decomposition) were compared with those obtained when samples were treated with the mixed acid after they were fused with sodium carbonate (which will be called alkaline fusion).

Since the amount of boron in rocks, which are not decomposed by the acid, can be determined with the alkaline fusion, the results, sometimes, vary considerably. In the authors' analytical results, samples which gave good agreements (between the alkaline fusion, and acid decomposition) were found to be those which left no discolored insoluble materials upon acid decomposition. Aside from those shown in Table I, although most of the igneous rocks were decomposed with the acid, most of the alluvial rocks required alkaline fusions.

It is advisable to carry out alkaline fusion whenever there is a doubt. /744

TABLE I. RESULTS OF DETERMINATION OF BORON IN ROCKS

| Types | Quantitative Values of Boron (ppm) | |
|---|---|---|
| | Acid Decomposition | Alkaline Fusion |
| Basalt, Miharayama Oshima | 31 | 31 |
| Diabase, W-1[a)] | 10 | 11 |
| Basalt, Izu Peninsula | 1.8 | 2.2 |
| Granite, G-1[(a)] | 1.5 | 1.5 |
| Granite, Chikubayama | 2.7 | 2.7 |
| Tertiary Shell Stone, Niigata Pref[b)] | 37 | 47 |
| Tertiary Shell Stone, (Different Layer From Above) Niigata Pref[b)] | 24 | 33 |

Note: a) Standard samples, American Geological Survey Bureau.
b) Samples from integrated research on chemical reactions of the alluvial process.

## 2.5 Recovery Experiment

In order to assess the reliability of the method, a recovery experiment was conducted by adding boron to rocks. Boron 1 μg (10 ppm) was added to basalt (Miharayama, Oshima), and was analyzed three times (Table II).

TABLE II. RECOVERY EXPERIMENT

| | Boron (ppm) | | |
|---|---|---|---|
| Content | 1 | 2 | 3 |
| Amount Added | 31 | 31 | 31 |
| Total | 10 | 10 | 10 |
| Measured Value | 41 | 41 | 41 |
| Recovered Value | 43 | 42 | 40 |
| Difference | 12 | 11 | 9 |
| | +2 | +1 | -1 |

The added and the recovered boron are in good agreement.

The recovery experiment was also conducted by adding boron to the same sample, and treating it with the alkaline fusion, with good results. The experiment was also conducted on rocks whose boron contents were less than 10 ppm, with satisfactory results.

Also, when the sample weight of the recovery experiment was changed to 0.05g, or when the amount of solution sampled from the discolored solution after decomposition was varied to 10 ml, there was no difference in the results within the error of analyses.

## 2.6 Precision

Eight analyses were made on basalt samples from Miharayama, Oshima. The standard deviations are shown in Table III.

Similar results were obtained with the alkaline fusions.

TABLE III. PRECISION

| Number | Boron (ppm) | Deviation |
|---|---|---|
| 1 | 29 | -2 |
| 2 | 31 | 0 |
| 3 | 31 | 0 |
| 4 | 30 | -1 |
| 5 | 32 | +1 |
| 6 | 30 | -1 |
| 7 | 31 | 0 |
| 8 | 33 | +2 |
| Average Value | | 31 ppm |
| Standard Deviation | | 1.3 ppm |
| % Deviation | | 4.2% |

## 2.5 Additional Comments

We will discuss the points which require caution in the procedure. When reagents are re-prepared, or when new polypropylene or platinum crucibles are used, the absorbance of the blank will sometime change. When samples are decomposed by heating on a water bath, they must be heated gradually, and also, the heating time must be constant i.e., 20 minutes. When a value of less than 0.1 μg (10 ppm) was obtained using Curve II in Figure 1, re-process the sample and dilute to 20 ml, and determine the value from Curve I in order to minimize the error. When the solution must be diluted to 20 ml, it is convenient to have a 20 ml mark on the separatory funnel. Changing the volume by ±2 ml hardly affected the quantitative values of boron. Appreciable change in volume will cause errors.

## 2.8 Conclusion

Determination of boron was conducted by treating the samples either directly or after alkaline fusion with sulfuric, and hydrofluoric acids. Boron was then converted to $BF_4^-$, and after adding methylene blue, it was extracted with dichloroethane. A standard procedure was established after the conditions were examined in detail. With this method, a wide concentration range, 0.5 ~ 100 ppm boron, can be analyzed to ±0.3 ppm when the concentration is less than 10 ppm, and ±1 ppm when the concentration is over 10 ppm. The procedure is relatively simple, nevertheless, care must be taken with the blank. The analysis time is approximately 1~1.5 hours. The absorbance of the blank increased considerably when sulfuric and hydrofluoric acids were heated in a platinum crucible. Normal values can be obtained with alkaline fusions. We will pursue the problem later.

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